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RADIATION DAMAGE IN FERROELECTRIC ROCHELLE SALT

ROBERT T. QUINN

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RADIATION DAMAGE IN

FERROELECTRIC ROCHELLE SALT

Robert T. Quinn

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* * * * *

ROBERT T. QUINN

RADIATION DAMAGE

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FERROELECTRIC ROCHELLE SALT

by

ROBERT T. QUINN

Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

United States Naval Postgraduate School
Monterey, California

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from the

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ABSTRACT

A study of ionizing radiation effects in rochelle salt has been conducted using the X-rays from a standard diffraction unit. The effects found show that the ferroelectric properties are changed markedly during a short exposure time. New observations, reported for the first time, suggest an explanation of the dielectric changes. These effects are a strain, produced apparently by an irradiation induced charge, sufficient to cause plastic deformation of the crystal as shown by slip marks. The biasing effect of the irradiation induced charge and the stress, as a result of the slip, are shown to cause the ferroelectric hystersis loop distortions and the final complete dissappearance of the ferroelectric behavior. These effects are apparent after relatively light irradiations and appear to involve only slight disruption of the chemical bonds in the crystals. The decomposition of the crystal as expected with additional irradiation has not been investigated.

The writer wishes to express his appreciation for the assistance, many helpful suggestions, and the encouragement given him by Professor John R. Clark, of the U. S. Naval Postgraduate School, during this investigation. He, also, wishes to thank Professor C. H. Rothauge, of the Electrical Engineering Department, and Mr. R. F. Edwards and W. D. Penpraze, of the Metallurgy and Chemistry Department, for their assistance in building and the designing the equipment used. He is indebted to Mr. R. S. Alger of the U. S. Naval Radiological Defense Laboratory, San Francisco for the Optical and Paramagnetic Resonance data.

TABLE OF CONTENTS

SECTION	TITLE	PAGE
1.	Introduction	1
2.	Ferroelectrics	3
3.	General Properties of Rochelle Salt Crystals	5
4.	Experimental	11
5.	Discussion	20
6.	Conclusions and Recommendations	25
7.	Bibliography	26

LIST OF ILLUSTRATIONS

Figure		Page
1.	Domains in Rochelle Crystals	27
2.	Dielectric Constant vs. Temperature Curve	28
3.	Effects of Pressure on Hystersis Loops	29
4.	Electrical Bridge Block Diagram	30
5.	Normal Hystersis Loop	31
6. - 16.	Loops from Irradiated Crystals	31-33
17.	Optical Transmission Spectra	34
18.	Microstructure of Half Irradiated Crystal	35
19.	Microstructure of Crystal Irradiated 28 Hours	35
20.	Strain vs Irradiation Time (Uninterrupted)	36
21.	Strain vs Irradiation Time (Interrupted)	37

INTRODUCTION

The physics of radiation and its effects on materials is a new field of vital importance to the materials engineer. The discovery of radioactive minerals and the production of the first X-rays at about the same time during the latter part of the nineteenth century first brought attention to radioactive radiation with its many dangers and uses. The first uses of nuclear fission to produce power in the last twenty years has intensified the problem of the interaction of radiation with materials. For the first time the engineer has become directly concerned with the effects of radiation on materials. A more thorough knowledge of the effects of radiation on engineering materials is needed by the engineer to design for the control and use of nuclear power.

Many studies have been and are being made of the effects of radiation on materials. To obtain any noticeable effects in most engineering materials, these experiments must be conducted where high radiation flux is available. Any installation which can give the great amount of radiation required is expensive to install and to maintain. Therefore any studies in this field which can be conducted without a powerful radiation source become attractive to anyone interested in radiation damage.

In some ferroelectric materials a relatively weak source of radiation such as an X-ray machine or portable Cobalt 60 source can be used to produce noticeable effects in a short exposure time. The effects which have been reported to date have dealt primarily with the dielectric changes. This material offers an opportunity for study

which does not require most of the costly equipment associated with radiation damage studies.

Studies of radiation damage in ferroelectric materials have been conducted by V. A. Iurin and I. S. Zheludrv[1] in Russia using a Cobalt 60 source and X-rays of an unspecified strength. In the United States, A. G. Chynoweth[2] conducted studies at Bell Telephoen Laboratories using a standard X-ray diffraction unit.

These reports demonstrated that some radiation damage experiments with ferroelectrics were possible at the U. S. Naval Postgraduate School. X-ray diffraction units were available as a radiation source and the other equipment required could be built easily and cheaply. It was proposed that studies be conducted to investigate why small amounts of radiation produce the dielectric changes in ferroelectrics.

(1) Bulletin of the Academy of Science of the USSR Vol. 20 pp 197 and Vol. 21, No. 3, pp 341.
(2) Phys Rev. Vol. 113 pp 159.

FERROELECTRICS

Ferroelectrics are an engineering material for the electronic industry. A ferroelectric is a material which exhibits a spontaneous polarization when placed in an electric field. Polarization is usually demonstrated in an electric circuit similiar to the circuit described latter in the paper. Most applications of ferroelectrics to date have been because of their piezoelectric properties and high dielectric constants, rather than the spontaneous polarization. They have been used as piezoelectrics in sonar transducers, pick-up crystals in microphones and phonographic turntables, and as capacitors in electrical circuits. Present interest in ferroelectrics is in developing them as storage elements for computers.

Valasek while studying the dielectric properties of rochelle salt first noticed the analogy of their dielectric hystersis loops with the hystersis loops of ferromagnetic materials.[3] This was the origin of the name ferroelectrics for these materials.

Ferroelectric materials are usually divided into several groups in accordance with their physical characteristics. The first group historically consist of tartaric acid salts which have a complex crystalline structure. Rochelle salt is the most familiar of this group. The second group consists of crystals with hydrogen bonds in which the motion of the proton is specifically connected with the ferroelectric properties. Potassium dihydrogen phosphate is the

(3) Ibid Vol. 19 pp 478

best known ferroelectric of this group. A third group consists of ionic crystals which have structures closely related to the perovskite and ilmenite structures. This is the simplest type structure to exhibit ferroelectric behavior. From this group, data on barium titanate is readily available. There are many other materials which are ferroelectric but very little information is available about them.

As in ferromagnetics the ferroelectrics have a Curie temperature which is the upper limit of their spontaneous polarization. In the case of rochelle salt there is also a lower temperature below which it is not ferroelectric.

Rochelle salt seemed to be the best choice of the ferroelectrics to study for several reasons. First, a large amount of work has been done with it, both experimental and theoretical, giving a wealth of facts to be used in this study. Second, the Curie temperature of rochelle salt was close to room temperature making the ferroelectric phase or the nonferroelectric phase easily observed. Finally, a supply of large uniform crystals was found which was readily available.

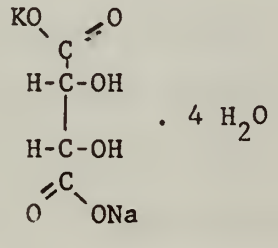
GENERAL PROPERTIES OF ROCHELLE SALT CRYSTALS

Pierre de la Seignette, an apothecary of La Rochelle, France, in 1672 produced a new salt of tartaric acid. This new salt, now commonly called rochelle salt, contained potassium substituted in one acid group and sodium in the other. The medical virtues and the chemical properties of rochelle salt became universally recognized by the late eighteen hundreds. The physical properties were first noted by the Curie brothers during their initial researches in piezoelectricity. The first quanitative measurements of the piezoelectric effect in rochelle salt were made by Pockels in 1894. He also was the first to report some of the anomolies in the dielectric properties in X cut crystals. When Valasek became interested in these crystals in 1921, they were fairly well known for their piezoelectric properties and some qualitative information on the dielectric properties had been published. He was the first investigator to report the presences of the two Curie temperatures between which rochelle salt crystals are ferroelectric.

Rochelle salt crystals are grown by two methods, crystallization by cooling and crystallization by evaporation. In the first method a saturated solution of the crystals is prepared and a seed crystal is then placed in the solution. The temperature is very slowly lowered a tenth of a degree at a time. Very large crystals have been grown by this method and large scale commercial processes use this principle. The second method requires equally as much care and control for good crystals. The solution, with its seed crystal,

is kept at a closely fixed temperature. The evaporation may take place in a dessicator or under vacuum. Crystals up to 2kg. have been grown by the first method and up to 200 grams by the second.

Rochelle salt or potassium sodium tartrate tetrahydrate is the potassium sodium salt of tartaric acid with four molecules of water of crystallization. The chemical structural formula is as follows:



As the structural formula shows the acid and consequently the salt are enantiomorphous. Only the dextro acid occurs in nature, although the levo form has been produced in laboratories. The crystals as normally obtained are of the right hand form since they are produced from the natural acid.

The specific, or perhaps better the structural unit, weight is 282.184. The density at 25°C. is 1.775 $\pm$ 0.003. The crystal changes to a mixture of sodium and potassium tartrates and their saturated solution at 55.6°C; at 58°C. these salts are completely dissolved in the water. This is called the "melting point" although cooling does not reproduce the rochelle salt but instead the separate potassium and sodium tartrates. The solubility of rochelle salt in water at 0°C. is 1.5 moles (420 g.) and at 30°C. it is 4.90 moles (1390 g.)

Since the crystal has water of crystallization, it has an appreciable vapor pressure. Although this is a factor to be kept in mind when working with rochelle salt crystals, unless unusual conditions are encourntered, dehydration should not occur. At room temperature, if the relative humidity is between 35 and 85 percent, the crystal should be stable. [2] Dehydration produces a coating of white powder on the crystal surfaces.

Although several investigators have reported on the thermal expansion coefficients of rochelle salt crystals, the most reliable data seem to be that of Vigness. (4) He reported the following coefficients of expansion:

X direction	12° to 35°C.	58.3×10^{-6}
Y direction	12° to 24°C.	35.5×10^{-6}
	24° to 35°C.	39.7×10^{-6}
Z direction	14° to 24°C.	42.1×10^{-6}
	24° to 35°C.	43.6×10^{-6}

The principal refractive indices (5) are: nx = 1.4954; ny = 1.4920; nz = 1.4900.

For many years rochelle crystals were classed as orthorhombic and structure determinations were based on this premise. Jaffe (6) in 1937 first proposed that the crystal becomes monoclinic between the two Curie temperatures (-18°C. to +23.7°C.) He suggested that

(4) Phys Rev. Vol. 48 pp 198.
(5) Landolt-Bornstien "Tabellen" for Na light at 20°C.
(6) Phys Rev. Vol. 51 pp 43.

the change was so slight that it could not be detected by X-ray diffraction means. As new techniques developed, several other investigators reported the existance of the monoclinic phase between the Curie temperatures.[7]

Unit cell demensions as given by Ubbelohde and Woodward [7] at 25°C. are: a = 11.891 ± 0.007A; b = 14.264 ± 0.008A; c = 6.225 ± 0.004A. Recent work at Pennsylvania State University by R. Pepinsky and his co-workers has indicated that certain small changes are needed in these parameters, but their results have not been published.

Rochelle salt is classified as space group number 18, P222 in the orthorhombic, nonferroelectric phases and as space group number 4, P211 in the monoclinic, ferroelectric phase.

The domain structure of most ferroelectrics is studied by using the polarizing microscope. The domain structure of barium titanate was studied as early as 1946 using this method. In rochelle crystals greater difficulty has been experienced in observing the domains. It was 1950 before J. Furuichi and T. Mitsui [8] reported seeing the domains in rochelle crystals by the polarized light method. A more complete report was published by the same authors two years later.[9] The parts of their work which is of interest in this paper are the orientation, size, and

(7) Proc. Roy Soc Vol. 185 pp 448
(8) Phys Rev. Vol. 80 pp 93
(9) Ibid Vol. 90 pp 193

movement in an electric field of these domains.

The mechanism of the domain formation is illustrated in figure 1, a and b. Above the Curie temperature the optical axis is parallel to the c (Z) axis. When the transformation from orthorhombic to the monoclinic phase occurs at 23.7°C., the crystal is twinned as shown in the second illustration. A rotation occurs about the a (X) axis giving slabs within the crystal which have different extinction angles when viewed with a polarizing microscope. In rochelle salt this mechanism can operate in either of two ways, a rotation of Z about X, or a rotation of Y about the X axis. This gives the two types of domains, Z domains, slabs which have their long dimension parallel to the Z axis, and Y domains. The Z domains seem to be the more stable type for two reasons. They are the more prevalent of the two types and surface polishing of a specimen in which both are present causes the Y domains to disappear in favor of the Z domains. In thick crystals both Y and Z domains are usually present at different levels in the crystal. The boundary between the two levels is explained by Furuichi and Mitsui to be as in figure 1 part c. Since rochelle salts are polarized in the X direction only, the domain structure can not be seen when viewed along the Y or Z axis. The largest domain width reported was 0.5 cm but most domains were about 10^{-3} cm. Domains were shown to grow by wall movement when an electrical field was applied.

Faces of polished specimens of rochelle crystals can be identified by moistening slightly and observing the etch pits formed. Faces normal to the X axis show striation like pits which are parallel to the Z axis. On faces normal to the Y and Z axis rectangular pyramids extend upward from the surface. [1]

Many investigators have reported on the piezoelectric effect in rochelle crystals. There are several good texts which cover this property more fully than a summary which could be included in this paper. (See bibliography)

The dielectric properties of rochelle salt are of primary interest to this paper. The spontaneous polarization effect is found in the X direction only. The dielectric constants for the Y and Z directions are normal, at room temperature these are: Y = 11.1; Z = 9.2. [1] The dielectric constant for the X direction changes with the temperature, pressure, and electrical field strength. The variation with temperature and field strength as reported by Mason [2] is shown in figure 2. The change of the dielectric constant with pressure is shown in a series of hystersis loops by Mueller. (Figure 3) The effect of pressure is believed to be a polarization caused by the piezoelectric properties. The measuring field is superimposed on this charge and the loop appears to be distorted and unsymmetrical. Crystals which are electrically biased during hystersis measurements show a similar effect.

I. EXPERIMENTAL

A. General

The specimens were cut from rochelle crystal 45°X plates obtained from Mare Island Naval Shipyard. These plates, produced by the Brush Development Company for use in sonar transducers, had been stored at constant temperature and humidity. The plates were too large (3.8 X 2.5 X .63cm) for irradiation by the X-ray diffraction unit. To cut them to size a distilled water and string saw was used. The wetted linen thread was driven by an electric motor at about 5 cm/sec. The rough cut specimens were dressed with a flat file and then polished using 320 grit grinding compound in mineral oil on plate glass. For optical observations an additional polish using rouge in mineral oil on plate glass was used to remove surface scratches. Specimens were not of uniform size in their final form but were approximately 2.5 X 1.5 X 0.2 cm, which was a convenient size for uniform irradiation and handling.

The specimens were irradiated using a copper X-ray tube operating at 50 KV and 20 ma. At a distance of 6 to 7 cm from the tube window the whole specimen could be located in the beam. At this location a ionization chamber type portable counting meter indicated a dosage rate of about 50 r/hr.

For the electrical measurements electrodes were coated on the X faces with acetone thinned silver paint, manufactured by Sunshine Scientific Instrument Company for use with analog computers. The electrical lead for the face toward the X-ray window was a narrow aluminum foil strip applied to the paint before it dried. On the face away from the window the crystal was attached by the silver paint to the upper arm of an inverted L shape copper plate which served as the second

electrical lead.

If the hystersis measurements are taken at room temperature (21 - 25°C.) the dielectric constant fluctuates with temperature. Near the Curie temperature the dielectric constant can change by 1000 stat-farads/cm for a one degree change in temperature. To insure a constant temperature the lower arm of the copper plate was placed in a container of ice and water. This maintained the crystal at 10 $\pm$ 2°C., well within the ferroelectric temperature range where the dielectric constant is stable.

Cooling the specimens below room temperature caused condensation on the copper plate and the crystal, making surface conduction possible. When a surface current started it would build up catastropically, completely destroying some specimen edges by melting. To protect from condensation, the crystal attached to the copper plate was chilled to 0°C. and dipped quickly in melted parafin. This gave a very thin coat without damaging the specimen by the hot parafin.

For hystersis measurements, handling the specimen after irradiation and prior to the measurement changed the results. The equipment was arranged so manipulation of the specimen was unnecessary after placing it in the X-ray beam.

B. Hysteris Measurements

The hystersis loops were presented on a Dumont type 208 oscilloscope. The input bridge circuit used was designed by Diamant, Drinck, and Pepinsky.[10] This bridge is designed to match the con-

(10) Rev. of Scientific Inst. Vol. 28 pp 30

ductivity and capacitance of the specimen. A block diagram for the circuit is given in figure 4. Figure 5 shows a normal hystersis loop using this equipment. (Note maximum polarization can be taken directly from this picture.) In other types of bridges the polarization magnitude has to be extrapolated from an S-shaped loop. Here the capacity of the specimen is matched by the compensating capacitance of the bridge flattening the loop top and bottom. The conductivity of the specimen is matched by the resistor bank, straightening the sides. The loop presented, when compensated correctly, gives a true indication of the polarization effect. The square type loop approaches the theoretically ideal polarization curve. The values of polarization can now be read directly from the oscilloscope by calibrating the amplification stages and the input voltages. A peak voltmeter, which can read values of either applied field or of polarization by using the designed switching arrangement, can also be calibrated to give values directly without interpolating values between oscilloscope markings. The bridge circuit was not calibrated for this study so the hystersis loops pictured are of qualatative value only. With the specimen sizes used, the capacitance settings were between 100 and 150 MMf. The maximum resistance setting was used for all crystals in the undamaged state. The electrical field applied was 60 cycles A. C. Voltage; 1000 to 1200 v/cm saturated all specimens.

Figures 6 - 9 show pictures of hystersis loops during irradiation. These particular pictures were chosen to show some of the general distortions which the loops develop when the crystal is exposed to X-rays. Figure 6 was taken after 10.5 hours of irradiation

and figure 7 is from the same crystal after 18.5 hours exposure. Figure 8 was from another crystal after 14 hours of irratiation. Another form of loop, figure 9, was observed after 25 hours of irradiation. This loop is similar to the hystersis loop of a polycrystalline rochelle capacitor. Each crystal seemed to follow its own sequences of loop distortion but all crystals followed the same broad course of increasing distortion to a final linear polarization. Distortions in the loops usually became apparent after four to six hours in the X-ray beam. The hystersis loops showed continuous changes in the ferroelectric behavior and after 30 to 40 hours all crystals had received a sufficient amount of radiation to lose their spontaneous polarization characteristics. This was indicated by a straight line showing a linear polarization characteristic pictured on the oscilloscope as in figure 10.

All hystersis loops in a series were observed without changing the compensating capacitance and resistance settings made for the undamaged crystals. Since the necessary field applied to produce the loops had an annealing effect in the early stages of the distortions and a damaging effect in the later, loop observations were made as fast as a picture could be taken. This precluded any resetting of the compensation to get a more nearly normal loop. Any attempts to change the settings before applying the field would have been an anticipation of the effects and results could not be considered as true values.

The effect of applied field on the crystal changed with the amount of irradiation. Until the final stages in the deterioration of the loop the voltage had an annealing effect. A loop would appear in an distorted form when the voltage was first applied, but if the voltage

was left on for longer than three minutes the loop began to return toward a normal appearance. After this annealing the crystal would continue to show a normal loop while the field was applied. Two or three hours time was required, with the field off, after annealing, before distortions were apparent again. After the crystal had been irradiated about 40 hours the effect of applied voltage appeared to be damaging rather than annealing. One crystal observed after irradiating for 41 hours showed a very distorted loop. The X-ray and electrical field were turned off and the crystal was not irradiated further. The specimen was left at room temperature for 64 hours, then the ice bath was refilled and one hour allowed for the crystal to come to temperature. The picture then appeared as shown in figure 11; within one minute the loop collapsed to a straight line. The field was turned off for one and a half hours, then reapplied. As shown in figure 12 the loop was now square but not saturated; the voltage was raised, and at 1450 v/cm the crystal was saturated. The voltage was lowered immediately to 1170 v/cm, the original saturating voltage for the crystal, and left on. In thirty minutes the loop had collapsed to a straight line. The loop decay progressed as shown by figures 12-16. In the final stage of ferroelectric breakdown the electrical field thus seems to aid in the destruction of the ferroelectric characteristics rather than anneal out the damage.

C. Photoelectric and Restivity Measurements

Some crystals irradiated for long times broke down and became conducting when the voltage was raised a few hundred v/cm above the

saturation value. The values at which this occurred was much less than the listed dielectric strength but none of the unirradiated crystals broke down under the voltage range available with our equipment about 600 v.

Since this change in conductivity might be, at least in part, due to photoelectricity an attempt was made to measure any photoelectric current using a microampmeter, with a sensitivity of one microampere and 675 v/cm applied voltage. No photoconductivity could be detected with this method when the specimen was placed in the X-ray beam.

An attempt was made to measure the resistivity using a wheatstone bridge. This data was not quanitative because the resistance was not ohmic. However, these measurements indicated that the resistance dropped from about 100 000 ohms to about 25,000 ohms in a thin specimen (0.15 cm thick) after 20 hours of irradiation.

D. Absorption Spectra

The color of the crystal changes from clear to yellow with irradiation. Several specimens, both clear and yellowed, were sent to the U. S. Naval Radiological Defense Laboratory, San Francisco, for a measurement of the optical absorption properties. Data received (Transcribed as figure 17) indicated that the yellow absorption band caused by irradiation begins at about 5000 A and extends through the ultraviolet to the characteristic absorption of rochelle salt at about 2400 A. Electron Paramagnetic Resonance measurements by Radiological Defense Laboratory, at liquid nitrogen temperature, indicated the presence of unpaired electrons in the irradiated rochelle crystals. These unpaired electrons are typical of trapped radicals in an irradiated organic material.

The single crystal specimens, even when thinned to 0.3 to 0.5 mm, were opaque to infrared wave lengths.

E. Microstructure

Observations with a polarizing microscope indicated no change with irradiation in the rotation of the plane of polarization in the X direction.

In making the above measurements striations were observed in the irradiated crystals which could not be seen in the unirradiated crystals. To be sure these striations were caused by the X-ray, a crystal was placed in the beam with half of it shielded by a small piece of lead. Striations appeared in the unprotected half but not in the lead shielded half. The resultant appearance of the crystal is shown at a magnification of 25X in figure 18.

To study the striations in more detail a series of crystals were irradiated from two to twenty-eight hours. The striations were first visible after four hours of irradiation. At lower magnifications (25 X to 50X) the number of lines does not change after the first eight hours of irradiation. At higher magnification (300X) the striations do not appear as single lines but as a series of short lines at various levels in the crystal. At the higher magnification these short lines appear to grow in length with additional irradiation after eight hours but no increase in the density of the lines could be distinguished.

The striations are in two directions, parallel to the Y and Z axes respectively. At first long irradiation time was thought to broaden the lines parallel to Z to a much greater extent than those parallel to Y. Figure 19 is a picture of a specimen after 28 hours

of irradiation before surface grinding. By grinding the crystal down and examining the interior it was seen that the broadening effect was confined to the areas near the surface.

The domain structure was examined to see if it had any relation to the striation. Both Y and Z domains were seen in unirradiated specimens. In these large crystals the domains were almost uniform in width. (About 10^{-3}cm). Only Z domains were seen in the irradiated, polished specimens and extended the width of the specimen. The distance between striations is about 10^{-2} cm giving a Z striation for about every 10 domain widths. The Y striations are perpendicular to the domains, the short lines crossing several domains.

F. Strain Measurements

Strain measurements during irradiation were made using resistance type strain gauges connected to a Baldwin-Lima-Hamilton type N indicator. Gauges, attached by Duco cement, were oriented on the specimen in the direction 45° from the Y and Z axes; for rochelle salt this is the direction of maximum piezoelectric strain. The crystals were mounted in the X-ray beam so they were free from confining stresses. The irradiation caused the crystals to elongate in one direction and contract in the perpendicular direction. Figures 20 and 21 are graphs of strain versus the time in the X-ray beam. Data plotted in figure 20 is for continuous irradiation. During the irradiation for figure 21 the X-rays were turned off after 11.5 hours and turned on again after several hours. There is a strain while the crystal is being irradiated but after reaching a peak value the values fall off. The crystal as a whole seems to be changing, as indicated by the parallel falling off of the lower readings when the irradiation is interrupted.

G. Miscellaneous Observations

Other effects observed in this study caused by irradiating rochelle crystals:

1. The irradiated crystals are more brittle
2. The surface becomes rougher
3. The tendency of the crystal to lose some of the water of crystallization when heated to 45°C. is increased.

DISCUSSION

The results of this investigation and previous studies of radiation damage in ferroelectric crystals indicate a change from a ferroelectric to a paraelectric (polarization is linearly increasing with the applied field) behavior. Only a small fraction of the radiation, which one would expect to be needed to destroy the molecular structure, is required for this change. Also, with a gradual accumulation of damaged molecules or cells within the crystal, the ferroelectric behavior could not be expected to continue through the initial stages, then rapidly switch to the paraelectric behavior. Further, a complete chemical bonding rearrangement would undoubtedly cause a more decisive change in the other characteristics of the crystal. It, therefore, seems logical to seek another explanation for the polarization anomolies. Other investigators have offered several postulates to explain these changes but, in all cases, these were incomplete in some respect.

Iurin[1] working with rochelle salt attributed the anomolies to the stresses introduced by the impurity decomposition products. He reported that the decomposition gases H_2, CO, CO_2, and CH_4 were given off when rochelle crystals are irradiated with gamma rays from a Cobalt 60 source. He states that the stress of the decomposition products trapped in the crystal apparently transforms the crystal to a different energy state with antiparallel domains. This leads to linear polarization in sub-critical field analogous to that in antiferroelectric crystals. This conclusion does not explain the changes caused by the electric field and it seems that a greater number of

decomposing ionizations would be required than can be expected from the amount of radiation used.

Iurin's conclusions appear to be influenced by the work of Eisner.[11] In growing rochelle crystals Eisner doped them with impurity atoms of copper, molybdenum, and boron. The hystersis loops from these crystals are similar to the split loops found in the irradiated crystals. He concluded that the anomolies were caused by the pinning effect of the impurity atoms on the domain walls.

Chynoweth[2] in the discussion of radiation damage in ferroelectric triglycine sulfate offers several possible methods of accounting for the anomolous loops but does not give any direct proof. He suggested that one of the following might be the explanation:

(1) A multiple hit process where several adjacent cells are damaged across a domain and destroy the dipole coupling. This will not explain the electric field effects on the anomolous loops.

(2) The build-up of local charge fields.

(3) The creation of an elastic strain.

Neither of the studies in radiation damage to ferroelectrics reported evidence of the strain and the striations discovered during the experimental part of this study.[12] These new phenomena, due to ionizing radiation, support a more complete explanation for the hystersis

(11) Bulletin of the Academy of Science of the USSR Vol. 21 No. 3 pp 341

(12) See footnote (4) Vigness reported a movement of the 021 plane in rochelle salt crystals which had been exposed to X-rays. This plane movement is probably the same as the strain reported in this paper as strain in the 45° direction.

loop anomolies and other effects in the irradiated ferroelectrics.

The strains are caused by the ionization of relatively few molecules. The charged radicals are trapped within the crystal faster than they can be neutralized, making the total number build up to an average peak value as the irradiation is continued. From the strain measurement curves (Figure 20 and 21) it is clear that the peak strain, and therefore the radiation induced charge, is a fairly constant value. The strain reaches a peak value and declines at a uniform rate. The reference state of the crystal from which the difference in strain is measured is declining at the same rate, so the total developed irradiation charge is the same.

Time required to build up the strain to its peak value is, within experimental error, the same time required for the first striations to appear. It seems clear, the striations are slip lines in the crystal caused by the strain. The direction of maximum strain is 45° to the Y and Z axes, therefore, it can be considered a shear on the planes normal to the Y and Z directions. Slip occurs in these planes only and acts to relieve the strains produced. Since electrically shorting the faces of the crystal during the irradiation does not appreciably lower the strain, the change apparently is isolated within the crystal. The total strain measured is the net result of these local charges. Decay of the charge when the X-rays are turned off is a leakage or other neutrallizing effect which takes approximately two hours. No evident leakage current can be detected from leads attached to electrodes on the faces.

As the irradiation continues the slip becomes great enough for a

formation of many small fragments within the large single crystal. It is the behavior of these many small blocks and the effective biasing of the radiation induced charge which causes the various anomolous hystersis loops. As the strain continues after slip, the blocks tend to rotate slightly about the X axis. The stresses build up as the blocks are forced further out of alignment. When the stresses from the two directions become great enough, linear polarization occurs. (Figure 3 illustrates the effect of a double restraining stress on the hystersis loops of rochelle crystals.)

The early anomolies in the loops begin to occur when slip starts. Rotation has not occurred to an extent sufficient to develop a great amount of pressure, but slip across the domains has broken the crystal into more domains and a greater critical field is required to polarize them. If the field is applied for a length of time the anomolies in the hystersis loop tend to anneal out. This is caused by the polarization due to the applied field aligning the blocks in parallel directions; when the field is removed, time is required for them to rotate again to their new reference energy state which strain has created. In the latter stages of damage the applied field is attempting to realign the blocks parallel, but some blocks are pinned more tightly than others, so the alternating field tends to increase the disorder and build the stresses.

Figure 9 is further indication of this multiple crystal behavior. In this instance the crystal had been irradiated for a total time of 25 hours and 12 hours had passed since the electrical field had been applied. The blocks seem to be completely misaligned but not far

enough to build up sufficient pressure to cause the linear polarization. This loop is similar to that from a small grain polycrystalline capacitor of rochelle salt.

Crawford and Wittels[13] reported a similar mosaic block effect in quartz, also piezoelectric, and other silicates subjected to neutron irradiation. These experiments, at Oak Ridge National Laboratories, used X-ray diffraction methods to detect this effect.

The brittle behavior of the irradiated crystals supplements the idea of an internal fragmentation. The greater tendency of the irradiated crystals to lose water of crystallization can be explained by the easy diffusion paths created along the block boundaries.

From the experiments, evidence indicates that coloring and surface roughening effects noted are not directly associated with the dielectric anomolies. The coloring apparently is caused by decomposition impurities trapped in the crystal, and the surface roughening by surface decomposition where the products escape as gases.

(13) Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7 pp 654

CONCLUSIONS AND RECOMMENDATIONS

The effects of X-rays on rochelle salt can be summarized as follows:

1. The hystersis loops become distorted.
2. A strain, apparently piezoelectric, is induced.
3. Striations within the microstructure can be seen.
4. The crystals become more brittle.
5. The tendency of the crystals to lose the water of crystallization is increased.
6. The crystal becomes yellow.
7. The surfaces become rougher.
8. The decomposition gases, H_2, CO, CO_2, and CH_4, are given off and probably other decomposition products are given off.

The ferroelectric anomolies have been explained by the discovery of the strain and the striations during this study. The build up of strain, because of the piezoelectric charge created by the ionizing irradiation, is causing the crystal to slip along planes perpendicular to the Y and Z axis. Additional strain causes the stresses on these blocks to build up until the blocks have a linear polarization response rather than a ferroelectric one.

It is recommended that other ferroelectric crystals be irradiated and studied to see if similar effects can be observed. In rochelle crystals further study is needed to determine the effect of pressure on the ferroelectric behavior, this probably could be checked by X-ray diffraction methods. Other studies giving more exact electrical measurements might better explain the apparent piezoelectric strains found.

BIBLIOGRAPHY

1. W. G. Cady, Piezoelectricity - McGraw-Hill (1946)

2. W. P. Mason, Piezoelectric Crystals and their Application to Ultrasonics - D. Van Nostrand (1950)

3. Helen D. Megaw, Ferroelectricity in Crystals - Methuen (1957)

4. A. G. Chynoweth, Radiation Damage Effects in Ferroelectric Triglycine Sulfate - Phys Rev. Vol. 113, pp 159-166

5. Proceedings of the International Conference on the Peaceful Uses of Atomic Energy - Vol. 7 (1956)

6. E. T. Jaynes, Ferroelectricity - Princeton University Press (1953)

7. English Translation - Bulletin of the Academy of Sciences of the USSR - Vol. 20 Number 2

8. English Translation - Bulletin of the Academy of Sciences of the USSR - Vol. 21 Number 3

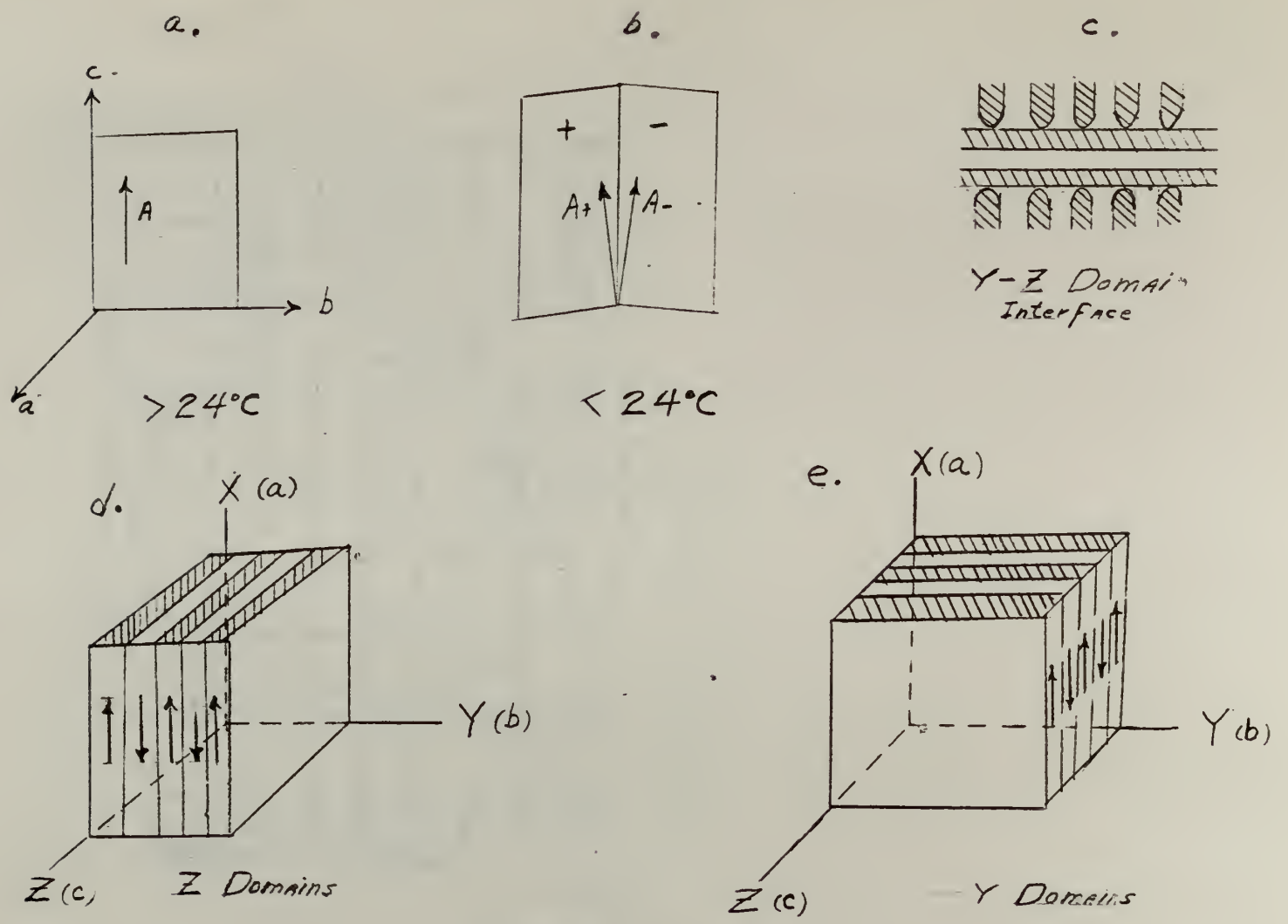

a.
c
A
b
a
>24°C
b.
+
−
A+
A-
<24°C
c.
Y-Z Domain Interface
d.
X (a)
Y (b)
Z (c)
Z Domains
e.
X(a)
Y (b)
Z (c)
Y Domains

Figure 1

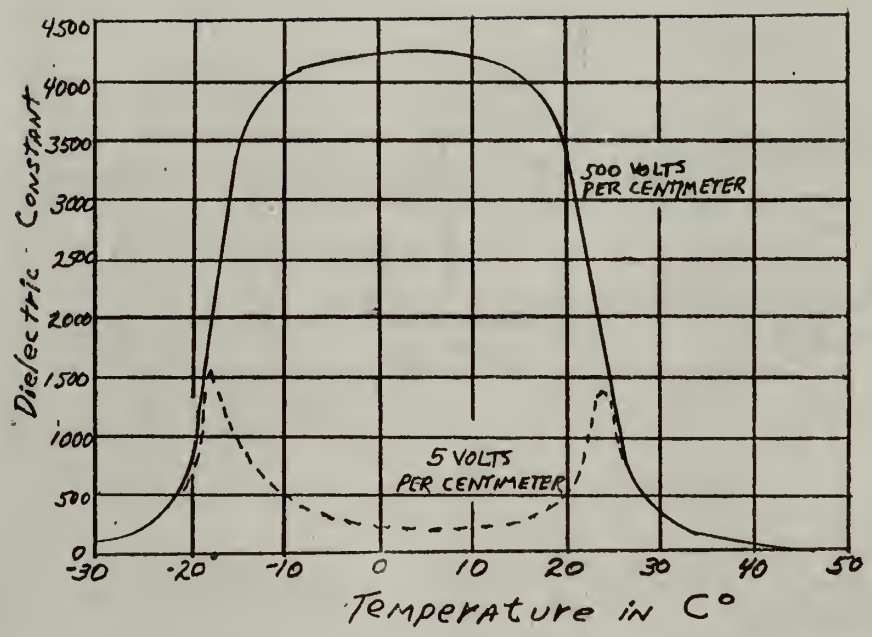
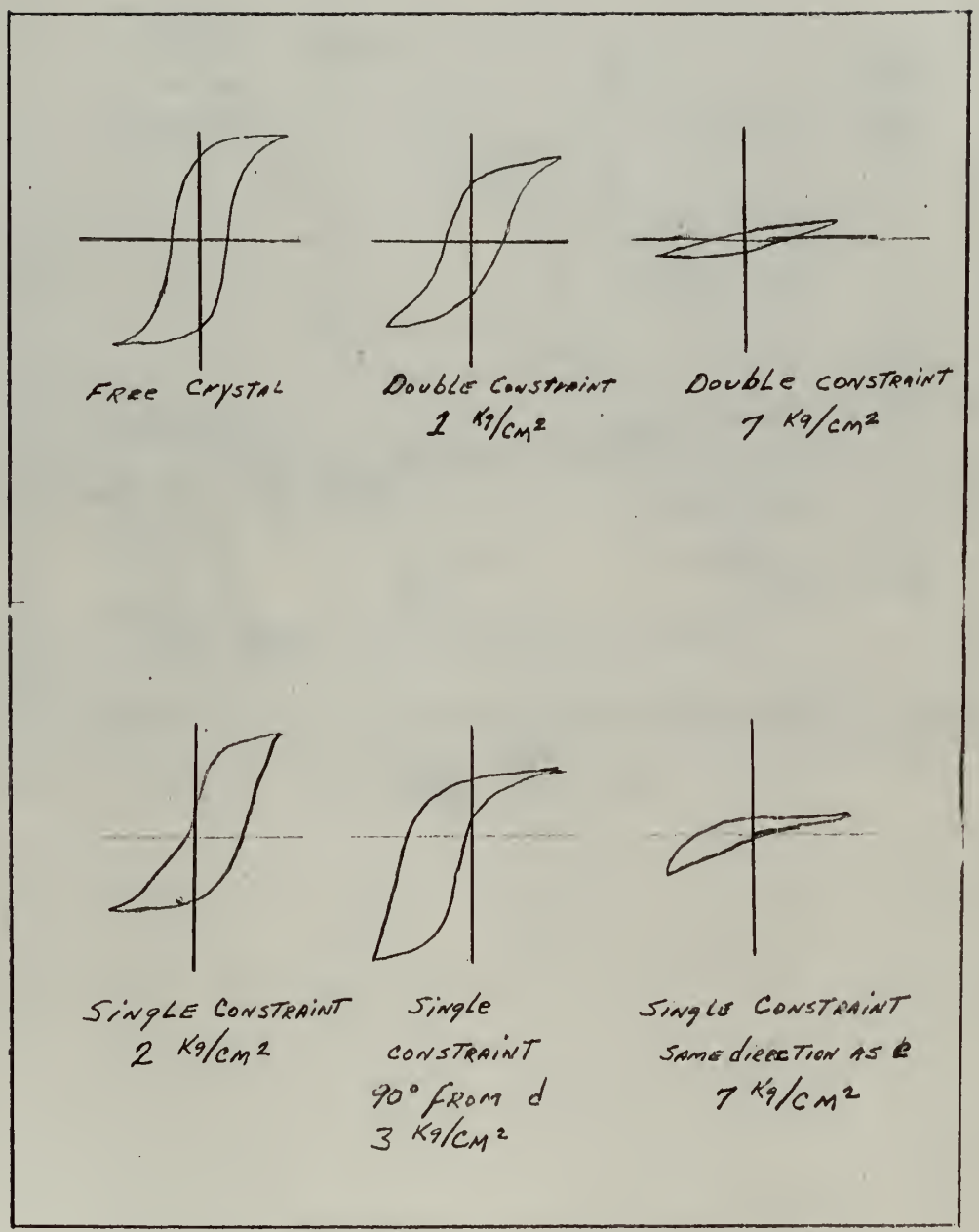
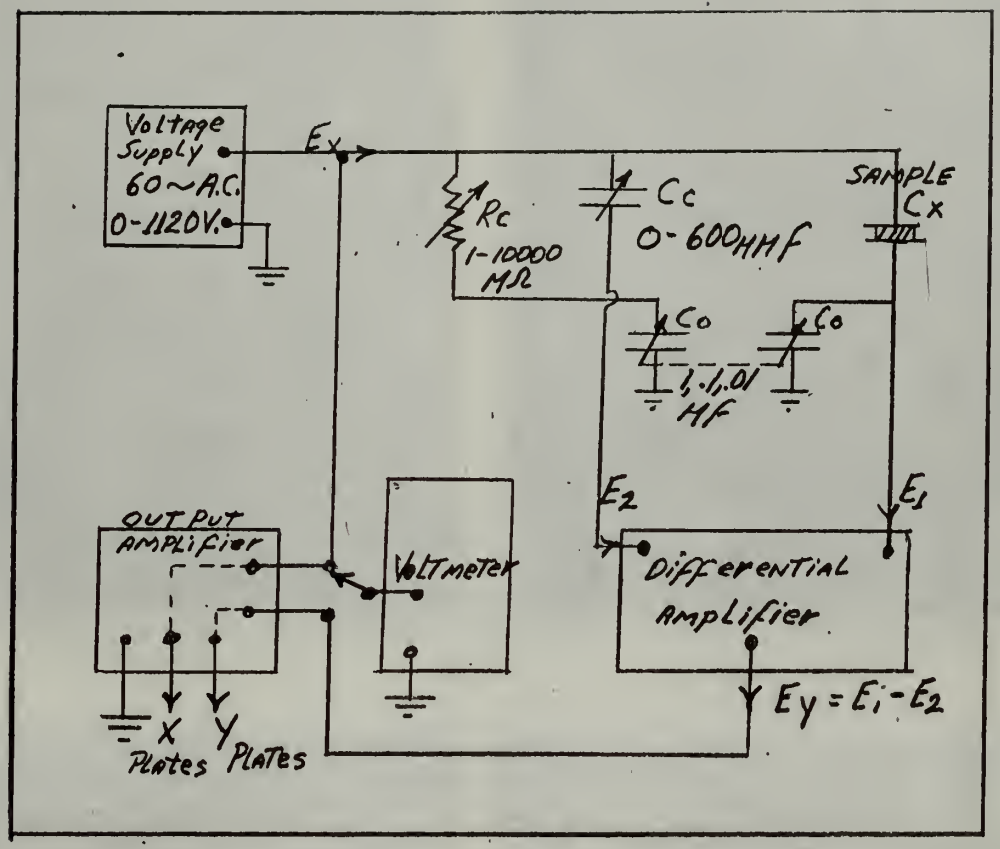

4500
4000
3500
3000
2500
2000
1500
1000
500
0
Dielectric Constant
500 VOLTS PER CENTIMETER
5 VOLTS PER CENTIMETER
-30
-20
-10
0
10
20
30
40
50
Temperature in C°

Fig 2



Effects of Mechical Contraint on the Hystersis Loops of Rochelle Crystals (From Mueller)

Fig 3


Voltage
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0-1120V.
Ex
Rc
1-10000
MΩ
Cc
0-600MMf
SAMPLE
Cx
Co
Co
1,.1,.01
Mf
E2
E1
OUT PUT
AMPLifier
Voltmeter
Differential
Amplifier
Ey = E1 - E2
X
Plates
Y
Plates

Fig. 4

FIG. 5

FIG.6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

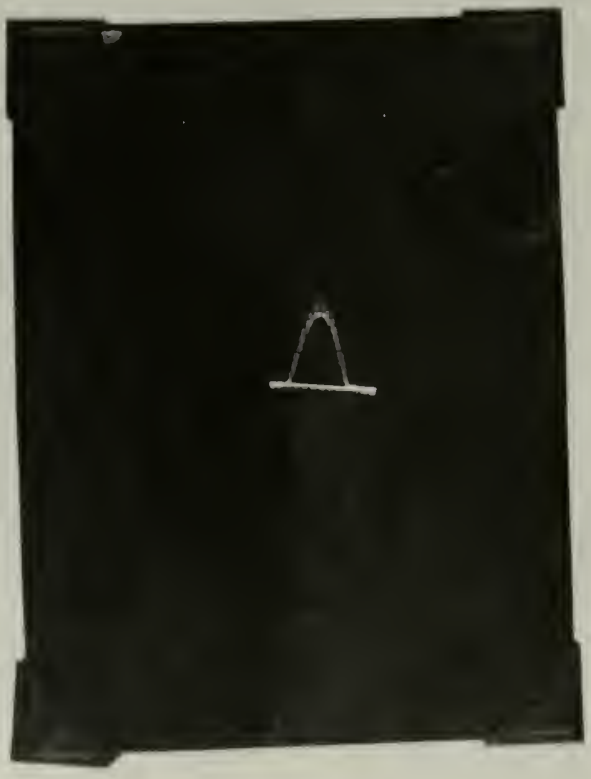


FIG. 16

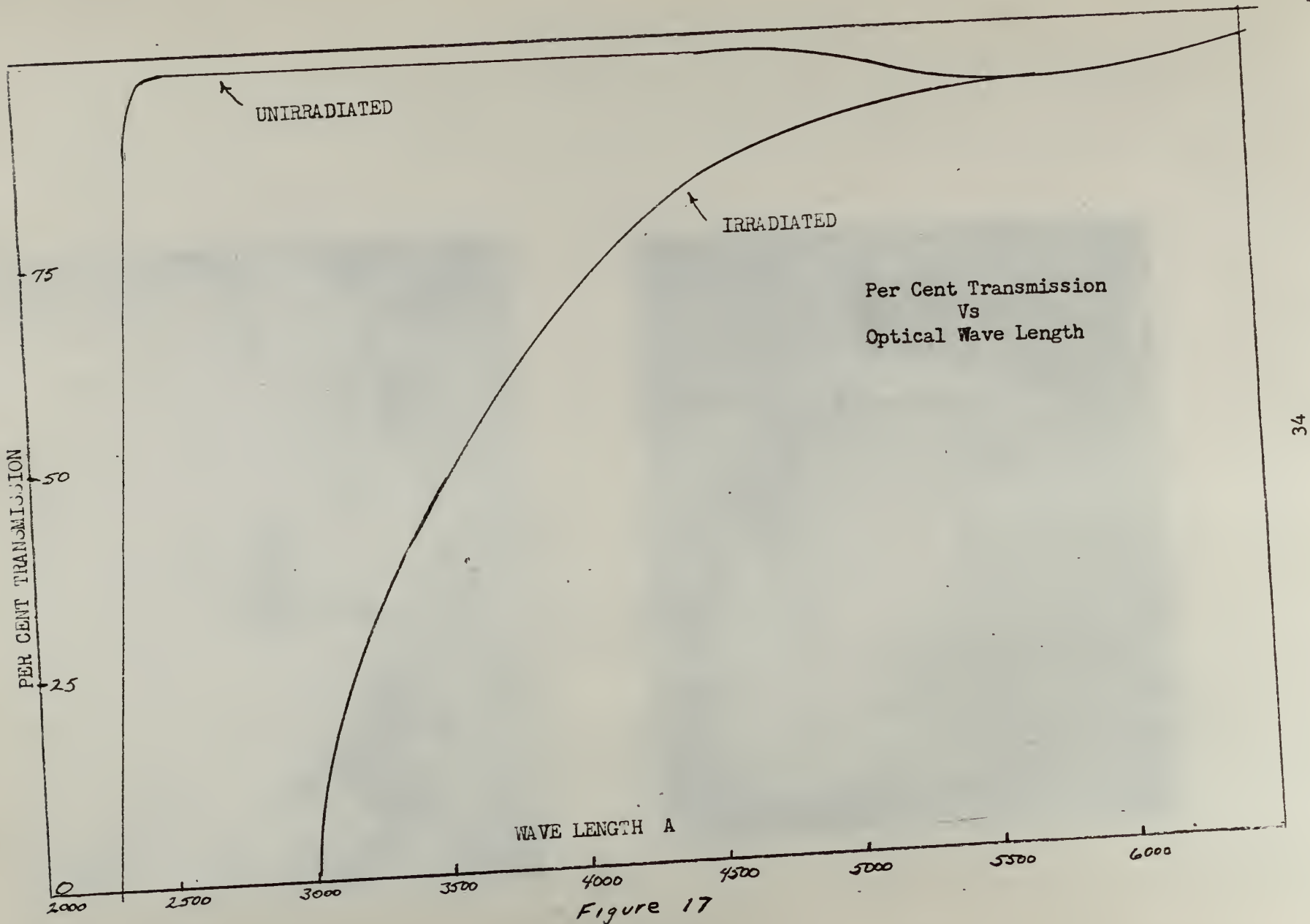
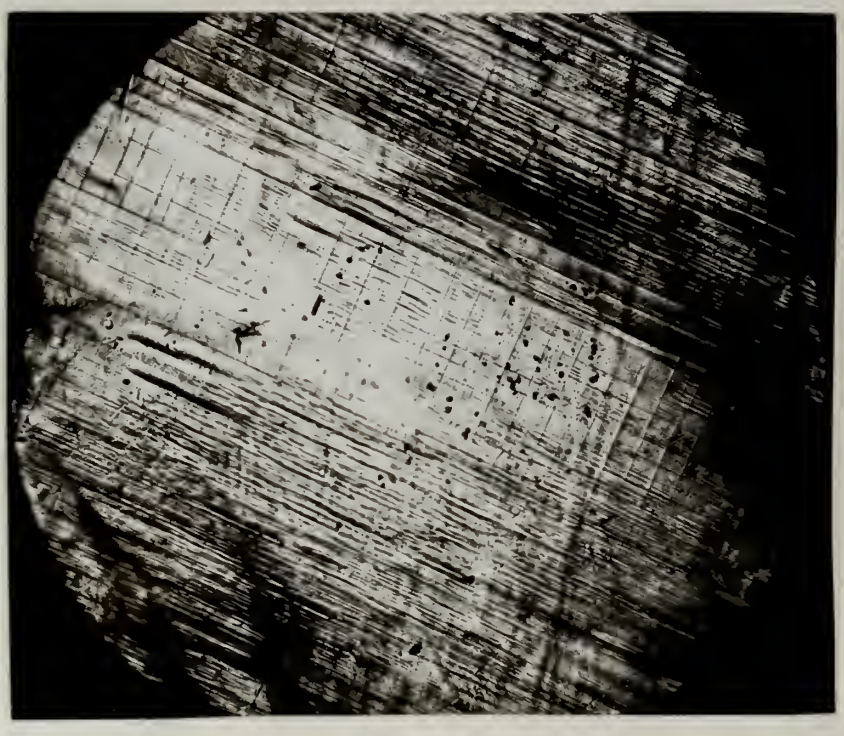

UNIRRADIATED
IRRADIATED
Per Cent Transmission
Vs
Optical Wave Length
PER CENT TRANSMISSION
75
50
25
0
WAVE LENGTH A
2000
2500
3000
3500
4000
4500
5000
5500
6000

Figure 17



140
120
100
80
60
40
STRAIN μ in/in
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28
Irradiation Time - Hrs

Figure 20

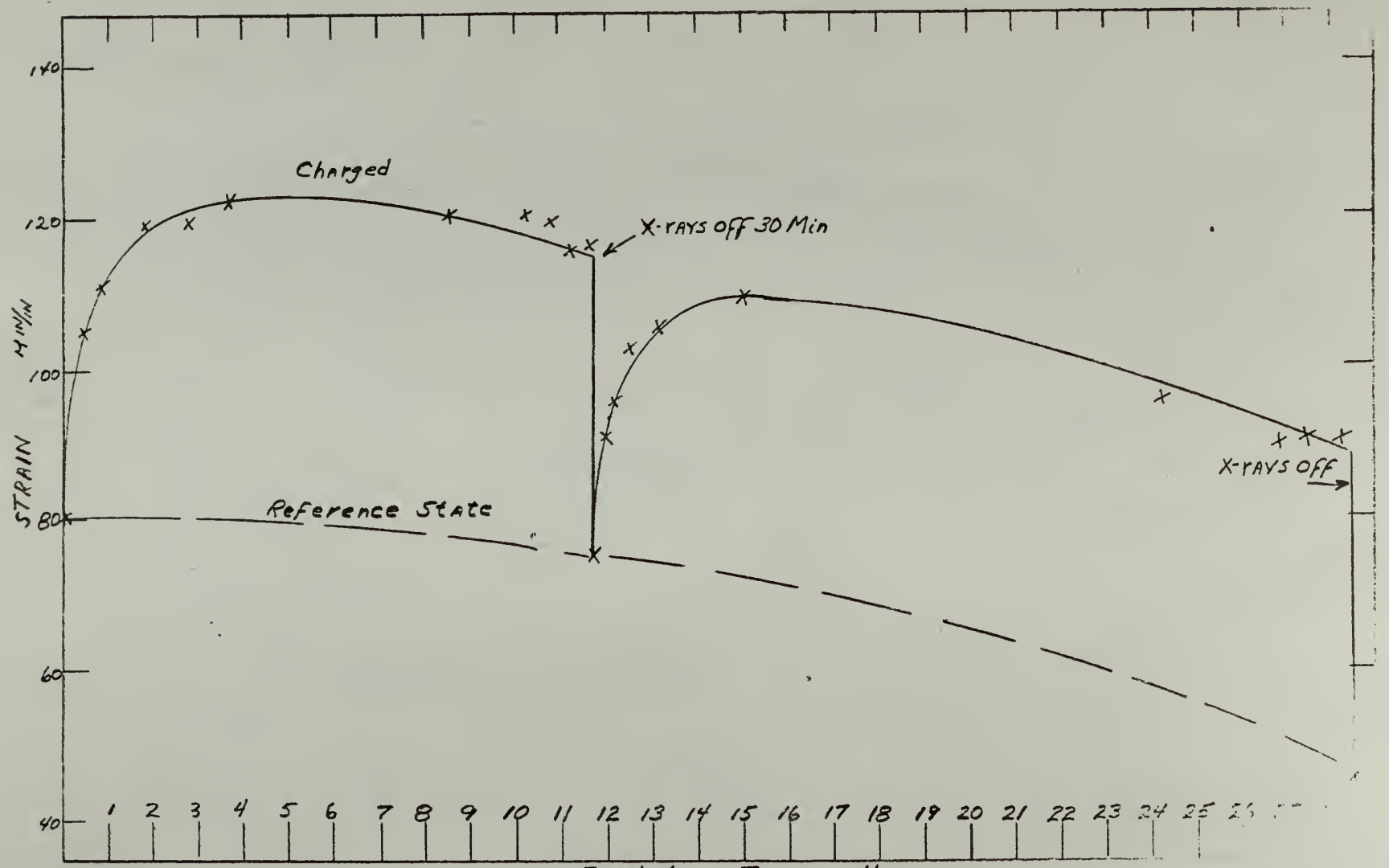

140
120
100
80
60
40
STRAIN μ in/in
Charged
X-rays off 30 Min
X-rays off
Reference State
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Irradiation Time — Hrs

Figure 21

thesQ7
Radiation damage in ferroelectric rochel
3 2768 001 93088 6
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